340 *J. Chem. Eng. Data* **2005,** *50,* 340−343

Isobaric Vapor−Liquid Equilibria of Binary Mixtures Containing the Carbonate Group −OCOO−

Yun-Jin Fang* and Jun-Ming Qian

UNILAB Research Center of Chemical Reaction Engineering, East China University of Science and Technology, Shanghai 200237, PR China

---

Isobaric vapor−liquid equilibria (VLE) data for the four systems of dimethyl carbonate + ethylene carbonate, methanol + ethylene carbonate, dimethyl carbonate + ethylene glycol, and ethylene glycol + ethylene carbonate containing the carbonate group −OCOO−, which exist in the process of synthesizing DMC by transesterification of ethylene carbonate with methanol, have been measured at atmospheric pressure or under vacuum in an Ellis equilibrium still. The experimental VLE data are thermodynamically consistent, and the activity coefficients have been evaluated with the Wilson and NRTL equations, showing that the systems of dimethyl carbonate + ethylene glycol and ethylene glycol + ethylene carbonate have stronger nonideality. The results of this work are useful to the research on DMC synthesis by transesterification.

Introduction

Dimethyl carbonate (DMC), an environmentally benign and biodegradable chemical, has attracted substantial research effort in recent years. It can be used to replace the acutely poisonous dimethyl sulfate as a methylating agent and phosgene as a carbonylating agent in the synthesis of many useful organic substances. Moreover, DMC is found to be an excellent gasoline additive for antibreaking and oxygen-content improvement,[1,2] and DMC can be used as a paint solvent replacing benzene, xylene, and so forth.[3]

At present, the main non-phosgene techniques of manufacturing DMC are the oxidative carbonylation route and the transesterification route. The technique of manufacturing DMC by transesterification based on methanol and propylene carbonate to coproduce a mole of useful glycol has developed greatly. For research on DMC's synthesis and application, vapor−liquid equilibrium (VLE) data of mixtures containing DMC are necessary.

Rodriguez et al. have reported the vapor−liquid equilibria of dimethyl carbonate with linear alcohols[4] and the VLE data of dimethyl carbonate with alkanes and cyclohexane[5] at 101.3 kPa. Luo and co-workers[6] have published the VLE data of alkyl carbonates with alcohols at 101.3 kPa, and Luo et al.[7] have also presented the VLE data for the binary systems of dimethyl carbonate + ethanol, dimethyl carbonate + diethyl carbonate, dimethyl carbonate + propylene glycol, and dimethyl carbonate + propylene carbonate under atmospheric pressure. Cocero et al.[8,9] have reported the VLE data of dimethyl carbonate + normal alkanes and dimethyl carbonate + cyclohexane, + benzene, or + tetrachloromethane. However, these VLE data are not needed by us.

In this work, isobaric VLE data under atmospheric pressure or vacuum are determined for the following binary systems: dimethyl carbonate (DMC) + ethylene carbonate(EC), methanol(ME) + ethylene carbonate, dimethyl carbonate + ethylene glycol(EG), and ethylene glycol + ethylene carbonate. These VLE data are not found in the literature.

Table 1. Antoine Coefficients[a] of the Pure Components

component	*A*	*B*	*C*
methanol[10]	7.19736	1574.99	−34.29
dimethyl carbonate[7]	6.4338	1413.0	−44.25
ethylene glycol[10]	7.9195	2615.43	−28.25
ethylene carbonate[10]	6.4897	1836.57	−102.23

[a] $\log P_i^S/\text{kPa} = (A - B)/(T/\text{K} + C)$.

Experimental Section

Chemicals. All of the chemicals used were purchased from commercial sources. Dimethyl carbonate was obtained with over 99.5% purity from Zibo Baoding Chemical Co., Shandong Province. Methanol and ethylene glycol are analytical-grade chemicals with a purity of greater than 99.8 wt %. Ethylene carbonate was fractionally distilled in advance in a vacuum distillation tower. The microwater content for each solvent was below 0.02 wt % measured by using the Karl Fischer method, which does not influence the vapor−liquid equilibria. Antoine coefficients of all pure components used in this paper are listed in Table 1.

Apparatus and Procedure. The vapor−liquid equilibrium measurement was carried out in an Ellis equilibrium still, which was described in detail by Li.[11] This still can be operated under atmospheric pressure or vacuum by reconstruction. In this Ellis still, both the liquid and condensed vapor phases are continuously recirculated to ensure that equilibrium is established rapidly. The equilibrium temperature was measured with a precision mercury thermometer with an accuracy of ±0.1 K and corrected by the dew point, indication, and pressure.[12] For the pressure measurement, a precision pressure gauge with an accuracy of ±0.01 kPa was used. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 30 min or longer. Then, samples of liquid and condensate were taken for analysis.

A model 7890 gas chromatograph (GC) supplied by Shanghai Techcomp Instrument Ltd. was adopted to

---

* To whom correspondence should be addressed. E-mail: yj.fang@163.com.

10.1021/je049859c CCC: $30.25 © 2005 American Chemical Society
Published on Web 01/19/2005

Table 2. Experimental Isobaric VLE Data of T, x_1, and y_1 and Experimental Activity Coefficients, γ_i, for the Binary Systems

P/kPa	T/K	x_1[a]	y_1[b]	γ_1[c]	γ_2
Dimethyl Carbonate (1) + Ethylene Carbonate (2)					
101.3	363.96	0.9711	0.9997	1.0102	3.3510
	364.97	0.9204	0.9993	1.0329	2.6690
	365.40	0.8791	0.9990	1.0671	2.4457
	368.25	0.7810	0.9982	1.1013	2.0486
	371.74	0.6296	0.9969	1.2307	1.7003
	375.27	0.5250	0.9959	1.3318	1.4336
	385.26	0.3623	0.9930	1.4615	1.0594
	401.21	0.2076	0.9844	1.6905	0.8886
	419.66	0.1190	0.9622	1.9033	0.8822
	446.95	0.0586	0.8807	2.0886	0.8608
	482.07	0.0231	0.6625	2.1592	0.8852
Methanol (1) + Ethylene Carbonate (2)					
101.3	414.75	0.0432	0.9589	2.2153	1.0011
	399.05	0.0680	0.9810	2.0945	1.0028
	372.78	0.1443	0.9954	2.0716	1.0134
	364.46	0.2011	0.9973	1.9298	1.0275
	357.96	0.2850	0.9950	1.6811	1.0600
	351.35	0.3920	0.9970	1.5363	1.1280
	349.96	0.4311	0.9991	1.4702	1.1626
	346.05	0.5370	0.9990	1.3581	1.2926
	344.24	0.6652	0.9995	1.1722	1.5565
	341.57	0.7282	0.9996	1.1828	1.7596
	341.36	0.8012	0.9998	1.0837	2.0841
	340.87	0.8530	0.9999	1.0370	2.4048
	339.56	0.9241	0.9999	1.0060	3.0403
Dimethyl Carbonate (1) + Ethylene Glycol (2)					
35.33	333.73	0.9523	0.9964	1.0357	11.6515
	334.02	0.8125	0.9956	1.1996	3.5558
	334.57	0.6113	0.9954	1.5610	1.7309
	335.49	0.4912	0.9950	1.8753	1.3552
	335.59	0.3523	0.9938	2.6017	1.3117
	335.67	0.2700	0.9943	3.3862	1.0645
	335.70	0.2591	0.9934	3.5215	1.2121
	336.56	0.1516	0.9912	5.8141	1.3364
	339.27	0.0911	0.9875	8.7164	1.4947
	355.49	0.0432	0.9752	10.3335	1.0795
	390.27	0.0152	0.8416	12.0093	1.0835
Ethylene Glycol (1) + Ethylene Carbonate (2)					
6.87	419.78	0.0214	0.265	4.9053	1.0139
	416.38	0.0332	0.3932	5.3665	0.9784
	413.23	0.0551	0.4780	4.462	0.9868
	408.46	0.0810	0.5791	4.4733	1.0108
	403.88	0.1801	0.6882	2.8996	1.0349
	401.88	0.3051	0.7150	1.9374	1.2255
	400.66	0.4452	0.7510	1.4701	1.4206
	399.61	0.5910	0.7767	1.1989	1.8168
	398.77	0.7112	0.8232	1.0954	2.1209
	398.16	0.8102	0.8638	1.0363	2.5604
	397.62	0.9402	0.9474	1.003	3.2218
	397.57	0.9658	0.9638	0.9955	3.8865
	397.55	0.9704	0.9724	1.0006	3.4271

[a] $x_i = (f_iA_i/\sum f_iA_i)$; x_i, mole fraction of component i for the liquid phase; A_i, peak area of component i by GC; f_i, relative correction factor of component i. [b] y_i, mole fraction of component i in the vapor phase. [c] γ_i, experimental activity coefficient of component i.

analyze the vapor and liquid samples, and the results were processed on a GC workstation. The column of the GC was a 2-m-long stainless steel pipe of 4-mm diameter and was filled with the 402 model organism monomer, which was (0.254 to 0.318)-μm white silicone bonded with dimethyl phthalate as a fixing agent. The detector was a TCD with hydrogen as the carrier gas. The flow rate of hydrogen was 45 mL·min^{-1}. The oven temperature was 180 °C, the column temperature was 220 °C, and the vaporizer temperature was 220 °C. The detection current was 150 mA.

Table 3. Parameters m and n of the MPR Equation for Pure Substances

component	m	n
dimethyl carbonate	0.9177	0.0819
methanol	1.2048	0.0903
ethylene glycol	0.9222	0.1871
ethylene carbonate	0.8101	0.1553

In the experiments on the systems of DMC + EG and EG + EC, water was found when T exceeded 433.15 K, especially in the vapor phase. This is because of the condensation of ethylene glycol producing water and diethylene glycol at high temperature. Therefore, VLE data of the systems containing ethylene glycol measured under vacuum are needed to decrease the temperature. The VLE experimental data for dimethyl carbonate + ethylene carbonate, methanol + ethylene carbonate, dimethyl carbonate + ethylene glycol, and ethylene glycol + ethylene carbonate are listed in Table 2, together with the experimental activity coefficients γ_i. The activity coefficients were calculated from[13]

$$\gamma_i = \frac{P y_i \varphi_i^{\mathrm{V}}}{x_i P_i^{\mathrm{S}}\ \varphi_i^{\mathrm{S}} \exp\left[\dfrac{V_i^{\mathrm{L}}(P - P_i^{\mathrm{S}})}{RT}\right]} \tag{1}$$

where, y_i and x_i are the experimental mole fractions in the vapor and liquid phases, respectively, P_i^{S} is the vapor pressure of pure component i estimated from the Antoine equation, V_i^{L} is the molar volume of pure component i, and φ_i^{V} and φ_i^{S} are the fugacity coefficients of component i in the mixture vapor phase and in the pure saturated vapor at temperature T, respectively, estimated by using the modified Peng−Robinson equation[14]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)} \tag{2}$$

$$a = \frac{0.45724(RT_{\mathrm{c}})^2}{P_{\mathrm{c}}\alpha(T_{\mathrm{r}})} \qquad b = \frac{0.778RT_{\mathrm{c}}}{P_{\mathrm{c}}}$$

$$\alpha(T_{\mathrm{r}}) = 1 + (1 - T_{\mathrm{r}})\left(m + \frac{n}{T_{\mathrm{r}}^{2}}\right)$$

where, P, T, and v are the system pressure (Pa), temperature (K), and volume (m^3·mol^{-1}), respectively, m and n are the empirical parameters fit to the saturated vapor pressure data of the pure components, listed in Table 3, and R is the gas constant.

Results and Discussion

The thermodynamic consistency of the experimental VLE data has been tested by the statistical method;[15] the VLE data does not verify the thermodynamic consistency when the grade of error of the experimental data is greater than VI. The results are listed in Table 4. As can be seen, the test is verified under the rule that the grade of error is less than VI.

In engineering design, the Wilson and NRTL equations are the most frequently used liquid-phase activity coefficient models. For the sake of ease of use, the experimental VLE data were correlated by Wilson and NRTL activity coefficient models for the liquid phase, and the vapor nonidealities were correlated by the MPR equation in calculating liquid-phase activity coefficients. The interaction parameters of the Wilson and NRTL equations were optimized by minimizing the objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{M}\sum_{j=1}^{N}[\ln \gamma_i^{\mathrm{exptl}} - \ln \gamma_i^{\mathrm{calcd}}]_j^2 \tag{3}$$

Table 4. Results of the Thermodynamic Consistency Test[a]

system	N	$x^2_{1-\alpha}(N-1)$	Q	grade of error
dimethyl carbonate + ethylene carbonate	11	18.31	8.18	III
methanol + ethylene carbonate	13	21.02	15.76	IV
dimethyl carbonate + ethylene glycol	11	18.31	13.62	IV
ethylene glycol + ethylene carbonate	13	21.03	19.07	IV

[a] N is the number of experiment data points, and $x^2_{1-\alpha}(N-1)$ and Q are statistical quantities under the rule.[13]

Table 5. Interaction Parameters for the Wilson and NRTL Models

	Wilson model				NRTL model				
systems	α_{12}	α_{21}	σ_T[a]	σ_{y_1}[b]	τ_{12}	τ_{21}	α_{ij}	σ_T	σ_{y_1}
DMC(1) + EC(2)	161.58	735.87	1.02	0.006	444.99	445.01	0.40	0.96	0.007
ME(1) + EC (2)	544.73	440.14	0.27	0.002	950.95	2.43	0.3112	0.23	0.002
DMC(1) + EG(2)	1032.23	2490.43	0.96	0.002	1282.04	1282.03	0.40	0.71	0.001
EG(1) + EC(2)	1355.04	332.29	0.11	0.002	203.36	1342.51	0.2898	0.10	0.001

[a] $\sigma_T = (\sum_{i=1}^{N}|T(\text{exptl}) - T(\text{calcd})|)/N$. [b] $\sigma_{y_1} = (\sum_{i=1}^{N}|y_1(\text{exptl}) - y_1(\text{calcd})|)/N$; N = number of data points.

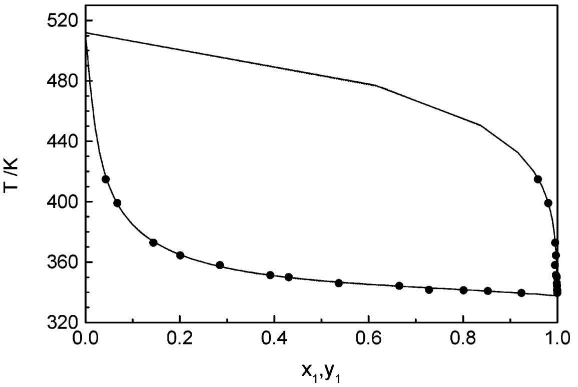

Figure 1. $T-x_1-y_1$ plots for the binary system methanol (1) + ethylene carbonate (2) at 101.325 kPa: ●, experimental points; −, calculated values from the Wilson model; - -, calculated values from the NRTL model.

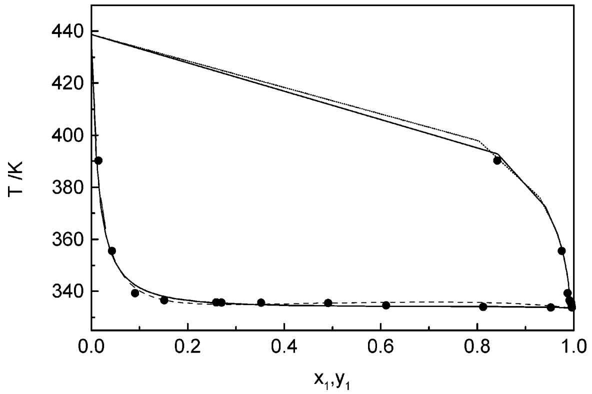

Figure 3. $T-x_1-y_1$ plots for the binary system dimethyl carbonate (1) + ethylene glycol (2) at 35.33 kPa: ●, experimental points; −, calculated values from the Wilson model; - -, calculated values from the NRTL model.

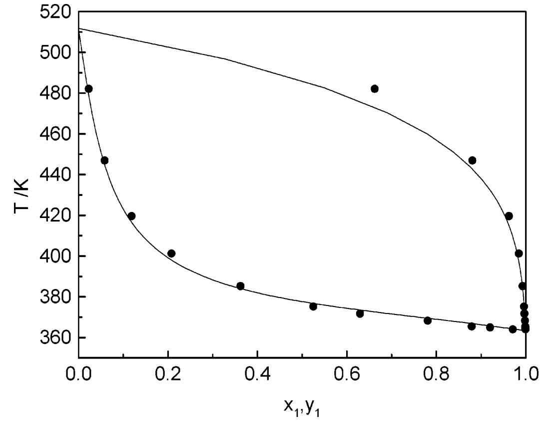

Figure 2. $T-x_1-y_1$ plots for the binary system dimethyl carbonate (1) + ethylene carbonate (2) at 101.325 kPa: ●, experimental points; −, calculated values from the Wilson model; - -, calculated values from the NRTL model.

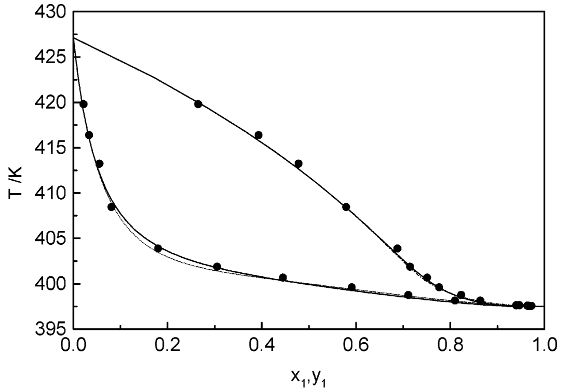

Figure 4. $T-x_1-y_1$ plots for the binary system ethylene glycol (1) + ethylene carbonate (2) at 6.87 kPa: ●, experimental points; −, calculated values from the Wilson model; - -, calculated values from the NRTL model.

where M is the number of components, N, the number of data points, and γ_i^{exptl}, the experimental activity coefficients. The fitted interaction parameters in both the Wilson and the NRTL equations are given in Table 5, together with the mean deviation σ.

Comparisons between the VLE data predicted by the Wilson and NRTL equations and the experimental data are shown in Figures 1−4. As can been seen, they agree very well.

Obviously, the systems of DMC + EC and ME + EC are close to ideal, with the maximum value of γ_i not exceeding 3.5. However, the system of DMC + EG shows strong nonideality because the maximum value of γ_i exceeds 10. The system of EG + EC also shows a strong deviation from ideality because the maximum value of γ_i exceeds 5.3. It can also be seen from Figures 4 and 5that an azeotrope is formed at 397.5 K with an ethylene carbonate mole concentration of 3.5% at 6.87 kPa.

Conclusions

Isobaric VLE data for four systems existing in the process of synthesizing DMC by transesterification of

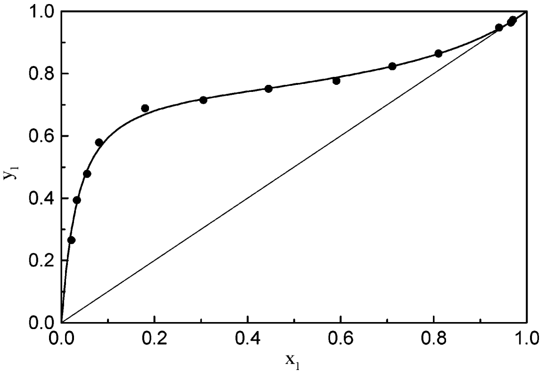

Figure 5. x_1–y_1 plot for the system ethylene glycol (1) + ethylene carbonate (2) at 6.87 kPa: ●,experimental points; −, predicted data from the Wilson equation in this work.

ethylene carbonate with methanol have been measured under atmospheric pressure or vacuum conditions. The experimental VLE data are thermodynamically consistent, and the activity coefficients have been evaluated with Wilson and NRTL equations, showing that the systems of dimethyl carbonate + ethylene glycol and ethylene glycol + ethylene carbonate have stronger nonideality.

A minimum-boiling azeotrope is exhibited in the binary system of ethylene glycol + ethylene carbonate, whose azeotropic temperature is 397.5 K at 6.87 kPa. The interaction parameters for the four binary systems of the Wilson and NRTL equations have been determined using our VLE data.

Literature Cited

(1) Pacheco, M. A.; Marshall, C. L. Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive. *Energy Fuels* **1997**, *11*, 2−29.

(2) Fang, Y. J.; Xiao W. D.; Lu, W. Z. Application Dimethyl Carbonate (DMC) as a Gasoline Additive. *Mod. Chem. Ind.* **1998**, *18*, 20−22 (in Chinese).

(3) Fang, Y. J.; Xiao W. D.; Zhu, K. H.; et al. Studies on Application of DMC as a Solvent to the Coating and Paint. *Paint Coat. Ind.* **2000**, *30*, 26−28 (in Chinese).

(4) Rodriguez, A.; Canosa, J.; Dominguez, A.; et al. Vapor-liquid Equilibria of Dimethyl Carbonate with Linear Alcohols and Estimation of Interaction Parameters for the UNIFAC and ASOG Method. *Fluid Phase Equilib.* **2002**, *201*, 187−201.

(5) Rodriguez, A.; Canosa, J.; Dominguez, A. et al. Isobaric Vapour-liquid Equilibria of Dimethyl Carbonate with Alkanes and Cyclohexane at 101.3kPa. *Fluid Phase Equilib.* **2002**, *198*, 95−109.

(6) Luo, H. P.; Xiao, W. D.; Zhu, K. H. Isobaric Vapor-liquid Equilibria of Alkyl Carbonates with Alcohols. *Fluid Phase Equilib.* **2000**, *175*, 91−105.

(7) Luo, H.-P.; Zhou, J.-H.; Xiao, W.-D.; Zhu, K.-H. Isobaric Vapor−Liquid Equilibria of Binary Mixtures Containing Dimethyl Carbonate under Atmospheric Pressure. *J. Chem. Eng. Data* **2001**, *46*, 842−845.

(8) Cocero, M. J.; Garcia, I.; Gonzalez, J. A. et al. Themodynamics of Binary Mixtures Containing Organic Carbonates, Part VI. Isothermal Vapor-Liquid Equilibria for Dimethyl Carbonate + Normal Alkanes. *Fluid Phase Equilib.* **1991**, *68*, 151−161.

(9) Cocero, M. J.; Mato, F.; García, I.; Cobos, J. C.; Kehiaian, H. V. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 2. Isothermal Vapor−Liquid Equilibria for Dimethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane. *J. Chem. Eng. Data* **1989**, *34*, 73−76.

(10) Luo, H. Z. *Handbook of Petrochemical Basic Data*; Chemical Industry Press: Beijing, 1982 (in Chinese).

(11) Li, W. Q. Study on the Synthesis of Dimethyl Carbonate by Transesterification. M.Sc Thesis, East China University of Science and Technology, Shanghai, China, 1996 (in Chinese).

(12) Zhou, W. J.; Chen, D. Y. *Wulihuaxue Shiyan yu Jishu*; ECICT Press: Shanghai, 1990 (in Chinese).

(13) Pransnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibra*; Prentice Hall: Englewood Cliffs, NJ, 1969.

(14) Liu, H. L.; Feng, G.; Hu, Y. A Modified PR Equation. *Tianranqi Huagong* **1987**, *1*, 47−50 (in Chinese).

(15) Hu, Y.; Ying, X. G.; Tang, X. H. Application of Statistical Theory in Studying Vapor-Liquid Equilibria, (1) Thermodynamic Consistency Test. *J. East China Inst. Chem. Technol.* **1984**, *2*, 205−213 (in Chinese).

Received for review April 5, 2004. Accepted November 23, 2004.

JE049859C